

Method for Producing Paper-based Composites and Water-adhesive  
Materials

This invention relates to a process for the production of at least two-layer (two-ply) paper laminates or moisture-tackifiable materials using water-soluble hotmelt adhesives and to the use of water-soluble high molecular weight polymers as a hotmelt adhesive for bonding paper, more particularly for bonding hygiene papers, or for the production of moisture-tackifiable materials.)

Hygiene papers are generally intended to be skin-friendly, i.e. they should produce little, if any, irritation of the skin when used on sensitive areas of the body. Besides control of the migratable ingredients of the hygiene papers, the subjectively perceived "softness" or "gentleness" of the hygiene papers plays a large part in the achievement of this effect. A particularly soft and gentle impression is normally achieved by the fact that the hygiene paper is made up of several thin layers. From the perspective of user friendliness, however, significant adhesion should exist between the individual layers to ensure that the hygiene paper does not immediately disintegrate into individual layers in use which would seriously affect its handling behavior. However, another trend in the manufacture of hygiene papers is to reduce of the number of layers required to obtain a soft effect as far as possible. The production and joining together of several layers is generally more expensive than the production of a hygiene paper reduced, for example, to only two layers.

In order nevertheless to achieve the velvety surface effect required, the surface of the hygiene papers is generally modified by embossing or other treatments which, for example, influence the orientation of the fibers on the fiber surface. Now, if an attempt is made to bond the individual layers of the hygiene paper using a water-soluble adhesive, several

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disadvantages are encountered. For example, water as a solvent for the adhesive has an adverse effect on the paper surface as reflected, for example, in creasing, shrinkage or smoothing of the paper surface. [All these effects have an unfavorable influence on the properties of the surface so far as a "gentle" feel to the user is concerned.]

Similar phenomena, such as creasing or shrinkage, also occur in the production of moisture-tackifiable materials, for example (stamps, envelopes or labels.)

In addition, the use of water-soluble adhesives in the bonding process necessitates a drying step in which water is removed from the bonded hygiene paper. Such drying steps are generally energy-intensive and add to the time and cost of the production process.

Another disadvantage of using water-soluble adhesives is that a relatively long period of time is generally required for the adhesion and cohesion values to guarantee adequate adhesion of the individual paper layers. This has an adverse effect on the subsequent processing of the bonded layers, i.e. the bonded paper layers only show adequate mechanical strength after drying.

Another requirement which adhesives used for bonding hygiene papers are expected to satisfy is that they should be completely soluble in water. This requirement is based on the large amounts of recycled paper used in the production of hygiene papers, i.e. production waste must be able to be directly reused in the production of new paper layers. To this end, the adhesive between the individual layers has to be completely removed from a recycled fiber slurry. Water-insoluble or substantially water-insoluble adhesive constituents, which can pass into the paper web from the recycled fibrous material during the production of a new paper layer, can lead to serious production failures. Corresponding adhesive residues normally form so-called "stickies" in the recycled paper webs, i.e. sticky spots which can lead to blocking of the paper web on rollers and

similar guide elements for the paper web. This normally results in tearing of the paper web and prolonged breaks in production. Accordingly, not only must the bond itself be reversible by water, leading to a dispersion of the adhesive in the water, the adhesive itself must be completely soluble in water. This prevents any adhesive residues discharged leading to stickies.

**EP-A 0 705 895** relates to a process for bonding tissue or nonwovens using a hotmelt adhesive composition containing up to 60% of a starch ester, up to 40% of a polar wax, up to 50% of a plasticizer, up to 25% of a tackifier and up to 3% of an antioxidant. Although this adhesive composition meets the basic requirements which an adhesive for bonding layers of hygiene paper is expected to satisfy, not all the constituents of the adhesive are completely soluble in water. This can lead to the above-described disadvantages in the recycling of such hygiene papers.

Accordingly, the problem addressed by the present invention was to provide a hotmelt adhesive for bonding layers of hygiene paper which could be applied as a melt, would lend itself to clean application even in the smallest quantities (less than  $0.1 \text{ g/m}^2$ ), would establish a strong, permanent and rapid bond between two paper webs to be bonded after they have been fitted together and, in addition, would be completely soluble in water, i.e. would be miscible with water in any quantity.

It has now been found that water-soluble polymers with a solubility in water at  $20^\circ\text{C}$  of at least 3% by weight do not have any of the disadvantages mentioned above.

Accordingly, the present invention relates to a process for the production of at least two-ply paper laminates in which a water-soluble hotmelt adhesive is applied to a first layer of paper and at least a second layer of paper is laminated onto the adhesive side of the first layer, the solubility of the hotmelt adhesive in water at  $20^\circ\text{C}$  being at least 3% by weight.

The process according to the invention is particularly suitable for

paper laminates intended for use as hygiene papers. ("Hygiene papers" in the context of the present invention are papers used primarily in the home, in communal facilities and for personal hygiene, for example kitchen roll, paper towels, paper handkerchiefs, paper napkins, toilet paper, diapers and the like.) The process according to the invention is particularly suitable for the production of paper laminates of tissue paper.

"Tissue paper" in the context of the invention is a particularly thin, soft, largely wood-free material, optionally with fine (dry) creping. The material is highly absorbent and generally has a weight per unit area as a single layer of  $> 25 \text{ g/m}^2$  (before creping). Toilet papers, paper handkerchiefs and cosmetic wipes are generally made from the tissue laminates obtainable by the process according to the invention.

"Hotmelt" adhesives in the context of the invention are adhesives which are solid at room temperature and at least substantially water- and solvent-free. Hotmelt adhesives are applied to the paper layers to be bonded from the melt and set physically, i.e. solidify, on cooling. Suitable hotmelt adhesives are, for example, organic polymers, such as polyesters, polyurethanes, polyamides, polyalkylene oxides, or polymers, for example polyacrylates. However, the hotmelt adhesives must satisfy at least the above-mentioned requirements in regard to solubility in water.

The term "polyacrylate" as used in the present specification applies in the following both to polymers or copolymers of acrylic acid or derivatives thereof and to polymers or copolymers of methacrylic acid or derivatives thereof.

Polyacrylates suitable as hotmelt adhesives in accordance with the present invention can be obtained by polymerizing acrylic acid or methacrylic acid or a derivative of acrylic acid or methacrylic acid, for example an ester of acrylic acid or methacrylic acid, with monohydric or polyhydric alcohols, on its own (in the case of acrylic acid or methacrylic acid) or in the form of a mixture of two or more thereof in known manner,

for example by radical or ionic polymerization. The polymers or copolymers should at all events have a percentage content of free acid groups or salts thereof with alkali metal, alkaline earth metal or ammonium ions which is so high that the polymer has a solubility in water at 20°C of at least about 3% by weight.

For example, polyacrylates in the form of homopolymers or copolymers may be used as the hotmelt adhesive in accordance with the present invention, these homopolymers or copolymers also containing styrene, styrenesulfonic acid, acrylonitrile; vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride and/or butadiene besides acrylic or methacrylic acid.

Other acrylates or methacrylates or mixtures thereof with one or more functional groups may optionally be present during the polymerization. Examples of these other (meth)acrylates are maleic acid, itaconic acid, butanediol diacrylate, hexanediol diacrylate, triethyleneglycol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol diacrylate, trimethylolpropane triacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl acrylate, propylene glycol methacrylate, butanediol monoacrylate, ethyl diglycol acrylate and monomers containing sulfonic acid groups, for example 2-acrylamido-2-methylpropanesulfonic acid.

In one preferred embodiment, the polyacrylates have a molecular weight of about 3,000 to about 50,000.

Also suitable for use as hotmelt adhesives in accordance with the invention are polyesters with a molecular weight of about 3,000 to about 50,000, for example polyesters obtained by reaction of low molecular weight alcohols, more particularly ethylene glycol, diethylene glycol, neopentyl glycol, hexanediol, butanediol, propylene glycol, glycerol or trimethylolpropane, with corresponding at least difunctional acids. Other polyhydric alcohols suitable for the production of polyesters are 1,4-

hydroxymethyl cyclohexane, 2-methylpropane-1,3-diol, butane-1,2,4-triol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, propylene glycol, dibutylene glycol and polybutylene glycol.

Suitable polyester polyols are obtainable, for example, by  
5 polycondensation. Thus, dihydric or trihydric alcohols or a mixture of two or more thereof may be condensed with dicarboxylic acids or tricarboxylic acids or a mixture of two or more thereof or reactive derivatives thereof to form polyester polyols. Suitable dicarboxylic acids are, for example, succinic acid and higher homologs thereof containing up to 16 carbon  
10 atoms, unsaturated dicarboxylic acids, such as maleic acid or fumaric acid, and aromatic dicarboxylic acids, more particularly the isomeric phthalic acids, such as phthalic acid, isophthalic acid or terephthalic acid. Suitable tricarboxylic acids are, for example, citric acid or trimellitic acid. Polyester polyols of at least one of the dicarboxylic acids mentioned and glycerol with  
15 a residual content of OH groups are particularly suitable for the purposes of the present invention. Particularly suitable alcohols are hexanediol, ethylene glycol, diethylene glycol or neopentyl glycol or mixtures of two or more thereof. Particularly suitable acids are isophthalic acid or adipic acid or mixtures thereof.

20 Other polyols suitable as polyol component for the production of the polyesters are, for example, diethylene glycol or higher polyethylene glycols with a molecular weight ( $M_n$ ) of about 100 to about 22,000, for example about 200 to about 15,000 or about 300 to about 10,000, more particularly about 500 to about 2,000.

25 Polyesters suitable for use as a hotmelt adhesive in accordance with the present invention include, in particular, the reaction products of polyhydric, preferably dihydric, alcohols (optionally together with small quantities of trihydric alcohols) and polybasic, preferably dibasic, carboxylic acids. Instead of free polycarboxylic acids, the corresponding  
30 polycarboxylic anhydrides or corresponding polycarboxylic acid esters with

alcohols preferably containing 1 to 8 carbon atoms (where they exist) may also be used. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic. They may optionally be substituted, for example by alkyl groups, alkenyl groups, ether groups or halogens.

- 5 Suitable polycarboxylic acids are, for example, succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylene tetrahydrophthalic anhydride, glutaric anhydride, maleic  
10 acid, maleic anhydride, fumaric acid, dimer fatty acid or trimer fatty acid or mixtures of two or more thereof. Small quantities of monofunctional fatty acids may optionally be present in the reaction mixture.

- The polyesters may be terminated, for example, by carboxyl groups. Polyesters obtainable from lactones, for example  $\epsilon$ -caprolactone, or  
15 hydroxycarboxylic acids, for example  $\omega$ -hydroxycaproic acid, may also be at least partly used.

- At all events, however, the polyesters must have a solubility in water at 20°C of at least 3% by weight. (The solubility in water may be achieved, for example, by using suitable water-soluble comonomers in the production  
20 of the polyester. To adjust the water solubility of the polyesters, it is recommended, for example, to use corresponding (sulfonated polycarboxylic acids,) for example sulfonated phthalic acid, isophthalic acid or terephthalic acid, or to use water-soluble polyether polyols, such as polyethylene glycol with a molecular weight ( $M_n$ ) of at least about 100, in  
25 the polycondensation reaction.)

Other suitable hotmelt adhesives are, for example, polyalkylene glycols with a molecular weight ( $M_n$ ) of at least about 1,000 which have a solubility in water at 20°C of at least about 3% by weight.

- 30 *Subst* Corresponding polyalkylene glycols are generally obtained by catalyst-assisted ring-opening polymerization of alkylene glycols.

The polymerization reaction is normally carried out starting from a so-called starter molecule. Suitable starter molecules are, basically, any compounds which are capable of opening epoxide rings, optionally in the presence of a suitable catalyst. Examples include primary, secondary or tertiary amines, primary, secondary or tertiary alcohols, thiols or carboxylic acids.

The polymerization is generally carried out using a basic catalyst. (Polyalkylene glycols obtainable by polymerization of ethylene oxide, optionally in admixture with C<sub>3-12</sub> alkylene oxides, are preferably used for the purposes of the present invention.) However, the maximum percentage content of higher alkylene oxides in the polyalkylene glycol should be gauged in such a way that the solubility in water (also referred to in the present specification as water solubility) at 20°C is at least about 3% by weight. Suitable polyalkylene glycols are, for example, polyethylene glycols containing C<sub>3</sub> or C<sub>4</sub> units or both which are obtainable, for example, by copolymerization of ethylene oxide with propylene oxide or butylene oxide or mixtures thereof. However, polyethylene oxide obtainable by polymerization of ethylene oxide is preferably used for the purposes of the present invention.

In one preferred embodiment of the invention, polyalkylene glycols obtained using primary, secondary or tertiary alcohols or mixtures of two or more thereof as starter molecules are used as the hotmelt adhesive.

Suitable starter molecules are, basically, any monohydric or polyhydric alcohols or mixtures thereof, although polyalkylene glycols prepared using a dihydric or trihydric alcohol, for example ethylene glycol, propylene glycol, butylene glycol, pentanediol, hexanediol, heptanediol, octanediol and higher homologs thereof, neopentyl glycol, glycerol, trimethylol propane, triethylol propane, pentaerythritol, glucose, sorbitol, mannitol or a mixture of two or more thereof as starter molecule, are preferably used for the purposes of the present invention.



The lower limit to the molecular weight of the polyalkylene glycols usable as hotmelt adhesive in accordance with the present invention is determined by the adhesive properties of the polyalkylene glycol. At all events, its molecular weight should be so high that adequate adhesion and cohesion of the hotmelt adhesive are guaranteed. In addition, the molecular weight of the polyalkylene glycols should be so high that they are no longer pressure-sensitive in their adhesion behavior.

Accordingly, the polyalkylene glycols usable as hotmelt adhesive in the process according to the invention generally have a molecular weight ( $M_n$ ) of at least about 1,000, for example of at least about 3,000 and, more particularly, of at least about 6,000.

The upper limit to the molecular weight is generally determined by application as a hotmelt adhesive and by the water solubility. Accordingly, the upper limit to the molecular weight should be such that problem-free application of the molten polyalkylene oxide by rolling on or spraying through standard nozzles in known manner is possible. In addition, the molecular weight of the polyalkylene oxide should only be so high that the required water solubility of about 3% by weight is guaranteed. Accordingly, the upper limit to the molecular weight is, for example, at about 100,000 and more particularly at up to about 50,000.

The polyalkylene glycols may be used individually, i.e. as a polyaddition product with the molecular weight distributions typically formed in base-catalyzed additions of alkylene oxides onto water or other starter molecules. However, mixtures of different polyalkylene glycols with different molecular weight distributions may also be used. In addition, it is possible to use polyalkylene glycols formed by addition of only one alkylene oxide compound onto a starter molecule. However, polyalkylene glycols obtainable by addition of various alkylene oxides may also be used. They may be both block copolymers and statistical copolymers.

In addition, polyurethanes with a molecular weight ( $M_n$ ) of at least

about 2,000, for example of about 5,000 or higher, and a solubility in water at 20°C of at least 3% by weight may also be used as a hotmelt adhesive for the purposes of the present invention. Both ionic and nonionic, water-soluble polyurethanes are suitable as hotmelt adhesives.

- 5 Polyurethanes suitable as hotmelt adhesives for the purposes of the preset invention are normally prepared by reaction of at least one polyisocyanate, preferably a diisocyanate, and a polyol component which preferably consists predominantly of diols. The polyol component may contain only one polyol although a mixture of two or more different polyols  
10 may also be used as the polyol component. Polyalkylene oxides for example, more particularly polyethylene oxide, are particularly suitable as the polyol component or at least as part of the polyol component.

- The term "ionic" means that the polyurethane contains ionic groups or at least groups ionizable in an acid/base reaction as solubilizers, for  
15 example carboxylate, sulfonate, phosphonate or ammonium groups.

- (The term "nonionic" accordingly means that the polyurethane does not contain any ionic groups as emulsifying groups, i.e. no carboxylate, sulfonate, phosphonate or ammonium groups.) The water solubility is attributable instead to the hydrophilic nonionic groups of the  
20 polyoxyethylene  $-\text{[CH}_2\text{-CH}_2\text{-O-]}_n\text{-}$ . These structural units are derived in particular from the polyethylene oxide preferably used as polyol component. However, polyethylene oxide in the present context encompasses not only polyaddition products of ethylene oxide with water or ethylene glycol as starter molecule, but also polyaddition products of  
25 ethylene oxide with other dihydric alcohols, for example butanediol, hexanediol or 4,4'-dihydroxydiphenylpropane. Mixtures of two or more different polyethylene oxides differing, for example, in their average molecular weight  $M_w$  or  $M_n$  or in both may also be used. Copolymers of ethylene oxide with higher alkylene oxides, for example with propylene  
30 oxide, may also be used as the polyol component providing they are

sufficiently soluble in water, i.e. more than about 3 g remains dissolved in about 100 g of water at 20°C over a period of about 6 months.

- Up to 10% by weight, preferably up to at most 5% by weight and more preferably up to at most 2% by weight of the polyethylene oxide in the
- 5 polyol component may be replaced by other diols which contain a hydrophobic moiety with a water solubility of at most 2 g/100 g water. The hydrophobic moiety is in particular an aliphatic or alicyclic structure containing 2 to 44 carbon atoms and more particularly 6 to 36 carbon atoms. The moieties in question may also contain aromatic structures.
- 10 Diols containing at least one primary OH group, more particularly 1,2- or  $\alpha,\omega$ -diols, are preferred. However, diols with vicinal OH groups are also suitable.

The polyethylene oxide in the polyol component preferably has a molecular weight ( $M_n$ ) of about 200 to about 20,000, more particularly of

15 about 1,000 to about 15,000, for example of about 1,550, 3,000, 6,000 or 12,000.

- ~~Sub E17~~ In addition, up to 10% and preferably from 0.5 to 5% of the (polyethylene glycol) may be replaced by (hydrophobic homopolymeric polyalkylene glycols) the alkylene group containing more than 2, preferably
- 20 3 or 4 carbon atoms. Their molecular weights are in particular in the range from 150 to 10,000 g/mole.

Specific examples of the hydrophobic diols containing pure CH residues and ether groups are polypropylene glycol (PPG), polybutylene glycol, polytetrahydrofuran, polybutadienediol, hydroxyl-terminated ethyl-

25 ene/butylene copolymers (for example KRATON LIQUID Polymer L-2203), hydrogenated polybutadienediol and (alkanediols containing 4 to 44 carbon atoms.) Preferred hydrophobic diols are polypropylene glycol, polytetrahydrofuran with a molecular weight of 150 to 10,000, preferably 200 to 4,500 and more preferably 250 to 1,000, 1,10-decanediol, 1,12-

30 dodecanediol, 1,12-octadecanediol, dimer fatty acid diol, 1,2-octanediol,

1,2-dodecanediol, 1,2-hexadecanediol, 1,2-octadecanediol, 1,2-tetradecanediol, 4,4-isopropylidene dicyclohexanol and isomer mixtures thereof, 4,8-bis(hydroxymethyl)tricyclo[5,2,1,0<sup>2,6</sup>]decanes and isomer mixtures thereof, 1,4:3,6-dianhydro-D-mannitol, 1,4:3,6-dianhydro-D-sorbitol, 1,16-hexadecanediol, bisphenol A and propoxylation and/or ethoxylation products thereof, more particularly with up to 30 EO units, and finally monofatty acid esters of glycerol with fatty acids containing up to 22 carbon atoms, for example glycerol monoesters of behenic acid, oleic acid, stearic acid, myristic acid. Mixtures of two or more of the hydrophobic diols may of course also be used.

In addition, 0 to 5% and, more particularly 0.2 to 2% of the polyethylene glycol may be replaced by alcohols of relatively high functionality, more particularly by triols, for example by glycerol, trimethylol propane, triethanolamine or ethoxylated or propoxylated variants thereof. Pentaerythritol may also be used. Ethoxylated or propoxylated variants of amines or aminoalcohols, for example starting from ethylenediamine, diethylenetriamine, and higher homologs thereof, for example aminophenol, N-2-aminoethyl piperazine, are also possible.

In order to obtain polyurethanes of particularly high molecular weight, high-purity diols should be used. To this end, the content of alkali and alkaline earth metal ions should be less than 500 ppm, preferably less than 150 ppm and more preferably less than 10 ppm. In addition, the water content should be below 0.5% by weight, preferably below 0.1% by weight and more preferably below 0.05% by weight, as determined by the K. Fischer method.

Besides the diols of the polyol component, diisocyanates are key constituents of the polyurethane suitable as the hotmelt adhesive. Diisocyanates are compounds with the general structure  $O=C=N-X-N=C=O$ , where X is an aliphatic, alicyclic or aromatic radical, preferably an aliphatic or alicyclic radical containing 4 to 18 carbon atoms.

Examples of suitable isocyanates are 1,5-naphthylene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), hydrogenated MDI (H<sub>12</sub>MDI), xylylene diisocyanate (XDI), tetramethyl xylylene diisocyanate (TMXDI), 4,4'-diphenyl dimethylmethane diisocyanate, di- and tetraalkyl

5 diphenylmethane diisocyanate, 4,4'-dibenzyl diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, the isomers of toluene diisocyanate (TDI), 1-methyl-2,4-diisocyanatocyclohexane, 1,6-diisocyanato-2,2,4-trimethyl hexane, 1,6-diisocyanato-2,4,4-trimethyl hexane, 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethyl cyclohexane

10 (IPDI), chlorinated and brominated diisocyanates, phosphorus-containing diisocyanates, 4,4'-diisocyanatophenyl perfluoroethane, tetramethoxybutane-1,4-diisocyanate, butane-1,4-diisocyanate, hexane-1,6-diisocyanate (HDI), dicyclohexylmethane diisocyanate, cyclohexane-1,4-diisocyanate, ethylene diisocyanate, phthalic acid-bis-isocyanatoethyl ester;

15 diisocyanates containing reactive halogen atoms, such as 1-chloromethylphenyl-2,4-diisocyanate, 1-bromomethylphenyl-2,6-diisocyanate or 3,3-bis-chloromethylether-4,4'-diphenyl diisocyanate. Sulfur-containing polyisocyanates are obtained, for example, by reaction of 2 moles of hexamethylene diisocyanate with 1 mole of thiodiglycol or

20 dihydroxydihexyl sulfide. Other important diisocyanates are trimethyl hexamethylene diisocyanate, 1,4-diisocyanatobutane, 1,12-diisocyanatododecane and dimer fatty acid diisocyanate. Particularly suitable diisocyanates are tetramethylene, hexamethylene, undecane, dodecamethylene, 2,2,4-trimethylhexane, 1,3-cyclohexane, 1,4-cyclohexane, 1,3- and 1,4-tetramethyl xylene, isophorone, 4,4-dicyclohexanemethane and lysine ester diisocyanate. Tetramethyl xylylene diisocyanate (TMXDI), more particularly the m-TMXDI obtainable from Cyanamid, is most particularly preferred.

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In order further to increase the molecular weight, (chain extension,) for example, may be carried out in known manner by first preparing

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prepolymers with excess diisocyanate and then extending them with short-chain aminoalcohols, diols or diamines or with water to increase molecular weight.

To this end, prepolymers are initially prepared with excess diisocyanate and are then (extended with short-chain diols) or diamines or with water. Specific examples of chain-extending agents include:

- saturated and unsaturated glycols, such as ethylene glycol or condensates of ethylene glycol, 1,3-butanediol, 1,4-butanediol, 2-butene-1,4-diol, 2-butene-1,4-diol, 1,2-propanediol, 1,3-propanediol, neopentyl glycol, hexanediol, bis-hydroxymethyl cyclohexane, dioxyethoxyhydroquinone, terephthalic acid-bis-glycol ester, succinic acid di-2-hydroxyethylamide, succinic acid di-N-methyl-(2-hydroxyethyl)-amide, 1,4-di-(2-hydroxymethylmercapto)-2,3,5,6-tetrachlorobenzene, 2-methylene-1,3-propanediol, 2-methyl-1,3-propanediol; 3-pyrrolidino-1,2-propanediol, 2-methylene-2,4-pentanediol, 3-alkoxy-1,2-propanediol, 2-ethylhexane-1,3-diol, 2,2-dimethyl-1,3-propanediol, 1,5-pentanediol, 2,5-dimethyl-2,5-hexanediol, 3-phenoxy-1,2-propanediol, 3-benzyloxy-1,2-propanediol, 2,3-dimethyl-2,3-butanediol, 3-(4-methoxyphenoxy)-1,2-propanediol and hydroxymethyl benzyl alcohol;
- aliphatic, cycloaliphatic and aromatic diamines, such as ethylenediamine, hexamethylenediamine, 1,4-cyclohexylenediamine, piperazine, N-methyl propylenediamine, diaminodiphenyl sulfone, diaminodiphenyl ether, diaminodiphenyl dimethyl methane, 2,4-diamino-6-phenyl triazine, isophoronediamine, dimer fatty acid diamine, diaminodiphenyl methane or the isomers of phenylenediamine;
- carbonylhydrazides or hydrazides of dicarboxylic acids;
- aminoalcohols, such as ethanolamine, propanolamine, butanolamine, N-methyl ethanolamine, N-methyl isopropanolamine, diethanolamine, triethanolamine and higher di- or tri(alkanolamines);

- aliphatic, cycloaliphatic, aromatic and heterocyclic mono- and diamino-carboxylic acids, such as glycine, 1- and 2-alanine, 6-aminocaproic acid, 4-aminobutyric acid, the isomeric mono- and diaminobenzoic acids and the isomeric mono- and diaminonaphthoic acids.

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However, the polyurethane is preferably produced by a single-stage process. In this process, all the starting materials are initially mixed in the presence of an organic solvent at a water content of less than 0.5% by weight. The mixture is heated for about 1 to 30 hours to a temperature of  
10 60 to 200°C, more particularly to a temperature of 80 to 180°C and preferably to a temperature of 100 to 150°C.

The reaction time can be shortened by the presence of catalysts.

Particularly suitable catalysts are tertiary amines, for example triethylamine, 1,4-diazabicyclo[2,2,2]octane (= DABCO), dimethyl benzyl-  
15 amine, bis-dimethylaminoethyl ether and bis-methylaminomethyl phenol. 1-Methyl imidazole, 2-methyl-1-vinyl imidazole, 1-allyl imidazole, 1-phenyl imidazole, 1,2,4,5-tetramethyl imidazole, 1-(3-aminopropyl)-imidazole, pyrimidazole, 4-dimethylaminopyridine, 4-pyrrolidinopyridine, 4-morpholinopyridine, 4-methyl pyridine are particularly suitable.

20 Organotin compounds may also be used as the catalysts. Organotin compounds are understood to be compounds which contain both tin and an organic residue, more particularly compounds which contain one or more Sn-C compounds. Organotin compounds in the broader sense include, for example, salts, such as tin octoate and tin stearate. Tin compounds in the  
25 narrower sense include above all compounds of tetravalent tin with the general formula  $R_{n+1}SnX_{3-n}$ , where n is a number of 0 to 2, R is an alkyl group or an aryl group and, finally, X is an oxygen, sulfur or nitrogen compound or a mixture of two or more thereof. R preferably contains at least 4 carbon atoms and, in particular, at least 8 carbon atoms. The upper  
30 limit is generally at 12 carbon atoms. X is preferably an oxygen compound,

i.e. an organotin oxide, hydroxide, carboxylate or ester of an inorganic acid. However, X may also be a sulfur compound, i.e. an organotin sulfide, thiolate or thioacid ester. Among the Sn-S compounds, thioglycolic acid esters above all are of interest, for example compounds containing the

5 following residues:

- S - CH<sub>2</sub> - CH<sub>2</sub> - CO - O - (CH<sub>2</sub>)<sub>10</sub>-CH<sub>3</sub> or

- S - CH<sub>2</sub> - CH<sub>2</sub> - CO - O - CH<sub>2</sub> - CH(C<sub>2</sub>H<sub>5</sub>) - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>3</sub>.

Compounds such as these satisfy another selection criterion: in a preferred embodiment of the invention, the molecular weight of the organotin  
10 compound should be above 250 and, more particularly, above 600.

Another preferred class of compounds are the dialkyl tin(IV) carboxylates (X = O-CO-R<sup>1</sup>). The carboxylic acids contain 2, preferably at least 10 and more preferably 14 to 32 carbon atoms. Dicarboxylic acids may also be used. Suitable acids are, for example, adipic acid, maleic  
15 acid, fumaric acid, terephthalic acid, phenyl acetic acid, benzoic acid, acetic acid, propionic acid and, in particular, caprylic, capric, lauric, myristic, palmitic and stearic acid. Specific examples are dibutyl tin diacetate and dilaurate and dioctyl tin diacetate and dilaurate.

Tin oxides and sulfides and thiolates may also be used in  
20 accordance with the invention. Specific compounds are bis-(tributyl tin)oxide, dibutyl tin didodecyl thiolate, dioctyl tin dioctyl thiolate, dibutyl tin bis(thioglycolic acid-2-ethylhexyl ester), octyl tin-tris(thioglycolic acid-2-ethylhexyl ester), dioctyl tin bis(thioethylene glycol-2-ethylhexoate), dibutyl tin bis(thioethylene glycol laurate), dibutyl tin sulfide, dioctyl tin sulfide,  
25 bis(tributyl tin)sulfide, dibutyl tin bis(thioglycolic acid-2-ethylhexyl ester), dioctyl tin bis(thioethylene glycol-2-ethylhexoate), trioctyl tin thioethylene glycol-2-ethylhexoate and dioctyl tin bis(thiolatoacetic acid-2-ethylhexyl ester), bis(S,S-methoxycarbonyl) tin bis(thiolatoacetic acid-2-ethylhexyl ester), bis(S,S-acetylmethyl) tin bis(thiolatoacetic acid-2-ethylhexyl ester),  
30 tin(II) octyl thiolate and tin(II) thioethylene glycol-2-ethylhexoate.



Other examples are dibutyl tin diethylate, dihexyl tin dihexylate, dibutyl tin diacetyl acetate, dibutyl tin diethyl acetyl acetate, bis(butyl dichlorotin)oxide, bis(dibutyl chlorotin)sulfide, tin(II) phenolate, tin(II) acetyl acetate and other  $\alpha$ -dicarbonyl compounds, such as acetyl acetone, 5 dibenzoyl methane, benzoyl acetone, ethyl acetoacetate, n-propyl acetoacetate, ethyl  $\alpha,\alpha'$ -diphenyl acetoacetate and dehydroacetic acid.

The catalyst is preferably added to the polyol. The quantity in which it is used is determined by its activity and by the reaction conditions and is preferably in the range from 0.001 to 0.5% by weight, based on the polyol.

10 However, the reaction is preferably carried out in the absence of a catalyst. The solvent, too, is also preferably omitted. "Solvents" in the present context are understood to be inert organic liquids with a boiling point below 200°C at normal pressure.

The reaction is preferably carried out in such a way that the ratio of 15 OH groups in the polyol component to NCO groups in the polyisocyanate is about 1.0 to about 2.0:1, more particularly about 1.05 to 1.8:1, for example about 1.1 to 1.7:1 or about 1.3 to 1.6:1.

Another method of introducing ion-forming structural elements is to react OH-terminated polyurethaneoligomers with dicarboxylic anhydrides. 20 These may contain in all 2 to 44 and preferably 2 to 12 carbon atoms between the bis-acyl groups, such as an alkylene, alkenylene or arylene group. Specific examples are succinic anhydride, glutaric anhydride, 1,2,3,6-tetrahydrophthalic anhydride and isomers thereof, phthalic anhydride, trimellitic anhydride, 7-oxabicyclo[2,2,1]hept-5-ene-2,3- 25 dicarboxylic anhydride, 5-norbornene-2,3-dicarboxylic anhydride and isomers thereof, diglycolic anhydride, maleic anhydride, dimethyl maleic anhydride, citraconic anhydride, itaconic anhydride, alkenyl succinic anhydrides, preferably those of which the alkenyl groups contain more than 2 carbon atoms, more preferably more than 5 and, most preferably, more 30 than 7 carbon atoms. Specific examples are n-octenyl succinic anhydride,

n-dodecenyl succinic anhydride, tetrapropenyl succinic anhydride, n-hexadecenyl succinic anhydride and n-octadecenyl succinic anhydride. The alkenyl chain may be linear or branched. In addition, mixtures of alkenyl groups with different numbers of carbon atoms may also occur. Mixtures of several anhydrides are also possible, although cyclic anhydrides are preferred.

A molar excess of isocyanates may also be used, in which case NCO-terminated oligomers are formed.

In general, NCO groups are not wanted in the end product. However, NCO groups may be used in order, for example, to introduce hydrophobic or ionic structural elements.

Hydrophobic structural elements may also be obtained by reaction of NCO-terminated oligomers with monools or monofunctional amines containing  $\geq 2$  carbon atoms, more particularly  $\geq 6$ ,  $\geq 10$  or  $\geq 16$  carbon atoms. Specific examples are polyethylene/butylene containing one OH group, for example with an OH equivalent weight of 3,600 (Kraton L 1203), 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 10-undecen-1-ol, 1-dodecanol, 1-tridecanol, 1-tetradecanol, 1-pentadecanol, 1-hexadecanol, 1-heptadecanol, 1-octadecanol, 9-cis-octadecen-1-ol, 9-trans-octadecen-1-ol, 9-cis-octadecen-1,12-diol, all-cis-9,12,-octadecadien-1-ol, all-cis-9,12,15-octadecatrien-1-ol, 1-nonadecanol, 1-eicosanol, 9-cis-eicosen-1-ol, 5,8,11,14-eicosatetraen-1-ol, 1-heneicosanol, 1-docosanol, 13-cis-docosen-1-ol, 13-trans-docosen-1-ol. The corresponding fatty amines may also be used as hydrophobicizing structural elements.

Finally, another method of introducing ion-forming structures is to react NCO-terminated oligomers with hydroxycarboxylic acids or aminocarboxylic acids containing alkylene, alkenylene or arylene groups, as in the case of the dicarboxylic anhydrides. Examples include glycolic acid, lactic acid, caproic acid and mandelic acid and also aminocaproic acid, aminododecanoic acid, glycine, alanine and phenyl alanine.

In one preferred embodiment of the invention, a nonionic polyurethane with a molecular weight ( $M_n$ ) of at least about 2,000, more particularly a nonionic polyurethane obtainable by reacting at least one polyisocyanate with at least one polyalkylene glycol with a molecular weight of at least 1,000, is used as the hotmelt adhesive.

The hotmelt adhesive may contain other additives, for example plasticizers, rheological additives, antioxidants, UV stabilizers, dyes, tackifier resins or pigments (filler).

The tackifiers used are, for example, hydrocarbon resins, more particularly C5 or C9 resins or C5-resin-modified C9 resins. In addition, resins based on pure hydrocarbon monomers, for example resins obtainable from the polymerization of mixtures of styrene,  $\alpha$ -methyl styrene and vinyl toluene, are suitable for use as tackifiers. The hydrocarbon resins mentioned may be partly or completely hydrogenated.

Also suitable for use as tackifiers are natural resins, such as balsam resin which is obtained, for example, from trees and tall oil resin which accumulates in the manufacture of paper. The natural resins may be used in the above-mentioned form as tackifiers although they may also be used after esterification with corresponding polyhydric alcohols as pentaerythritol esters, glycerol esters, diethylene glycol esters, triethylene glycol esters or methyl esters.

Polyterpene resins are also suitable as tackifiers. Terpenes accumulate in the separation of resin acids from their natural solvents and may be polymerized to polyterpene resins. The terpene-phenol resins obtainable by phenol modification from polyterpene resins are also suitable for use as tackifiers.

The additives may be present in the hotmelt adhesive either individually or in the form of a mixture of two or more of the substances mentioned. The additives should be used in a quantity not exceeding about 20% by weight (based on the hotmelt adhesive as a whole). Suitable

quantities are, for example, quantities of about 0.1 to about 15% by weight or of about 1 to about 10% by weight. In a preferred embodiment of the invention, the additives are used in quantities of, for example, about 2, 3, 4, 5, 7 or 9% by weight.

- 5           The polyalkylene glycol advantageously has a melt viscosity of no more than 20,000 mPa.s (Brookfield Thermocell, spindle 27, 180°C). In a preferred embodiment of the invention, however, the melt viscosity is below that value, for example about 1,000 mPa.s to about 10,000 mPa.s, for example about 2,000 to about 8,000 mPa.s. Good results are obtained, for  
10   example, with viscosities of, for example, about 5,000 to 6,000 mPa.s for a melting temperature of about 150°C (Brookfield Thermocell, spindle 27).

- The hotmelt adhesives used in the process according to the invention should generally have a viscosity which enables them to be applied by standard methods. Accordingly, the hotmelt adhesives  
15   advantageously have a viscosity (Brookfield Thermocell, spindle 27) in the range from about 400 mPa.s at 100°C to about 20,000 mPa.s at about 180°C. In a preferred embodiment of the present invention, the hotmelt adhesives have a viscosity in the above-mentioned range at a temperature of from about 120°C to about 150°C. Suitable viscosities are, for example,  
20   about 1,000 to about 15,000 mPa.s or about 3,000 to about 8,000 mPa.s.

- 5063 → The process according to the invention for the production of at least two-ply paper laminates generally comprises at least one step in which hotmelt adhesive is applied to a first layer of paper and a second layer of paper is laminated onto the first layer after a certain time and spatial  
25   interval. To ensure adequate adhesion is developed between the first and second layers of paper, the hotmelt adhesive must still be sufficiently tacky at the time the second layer is laminated onto the first, i.e. it should not yet be physically cured. The period after application of the hotmelt adhesive in which the adhesive has sufficient tackiness for a second layer of paper to  
30   be laminated onto the first is referred to hereinafter as the "open time". By

"sufficiently tacky" is meant a tackiness which produces a bond between the paper layers with a peel strength of more than 0 N/cm.

At typical machine speeds of, for example, up to 600 m/min., it is generally sufficient if the hotmelt adhesive has an open time of about 0.1 to about 1 second, for example about 0.2 to about 0.5 second. If the hotmelt adhesive is only to be used when the machine has reached its full speed, an open time of the order mentioned above is generally sufficient. However, if the hotmelt adhesive is intended to lead to the bonding of at least two layers of paper during the startup phase of the machine, for example, the open time should be longer than indicated above. In that case, open times of about 1 to about 10 seconds, for example about 2 to about 8 seconds or about 4 to about 6 seconds, are advantageous.

In a preferred embodiment of the invention, the hotmelt adhesive is not pressure-sensitive, i.e. the surface of the hotmelt adhesive is no longer tacky after the end of the open time.

The hotmelt adhesive to be used in the process according to the invention is soluble in water so that a quantity of at least about 3% by weight dissolves completely in water at 20°C. By "complete dissolution" is meant the formation of a dispersion which is not tacky in the subsequent recycling process, if any, but preferably a molecularly disperse solution of the adhesive in water.

As mentioned in the foregoing, the hotmelt adhesives used in the process according to the invention are intended, for example, to simplify the recycling of already bonded paper layers into the stock circuit for the production of new paper layers. To this end, water is generally added to the already bonded layers of paper, dissolving the hotmelt adhesive and at the same time producing a fiber slurry suitable for further processing. This water generally has a temperature above the ambient temperature, for example in the range from about 25 to about 80°C. In this connection, it can happen that certain polymers suitable as hotmelt adhesives are no

longer sufficiently soluble in water at elevated temperature. The property which certain macromolecular compounds have of precipitating from a solution of the macromolecular compounds on heating is generally known as the upper critical solution temperature (UCST). This phenomenon  
5 generally manifests itself in visible clouding through the agglomeration of molecules no longer in solution.

Equally, certain macromolecular compounds can also have a lower critical solution temperature (LCST). This means that dissolved macromolecular compounds precipitate from their solution when its  
10 temperature is reduced. The solution is again clouded in this way.

Accordingly, in the interests of better observability, the term "cloud point", i.e. the point at which measurable clouding of the aqueous solution of the hotmelt adhesive can be observed, is used in the present specification. By "upper cloud point" is meant the clouding resulting from a  
15 UCST of the hotmelt adhesive whereas "lower cloud point" means the clouding resulting from an LCST.

If, for example, the hotmelt adhesive used consists of different polymers and if at least one of the polymers has a UCST and at least one of the polymers an LCST, an aqueous solution of this hotmelt adhesive has  
20 both a lower cloud point (caused by the LCST) and an upper cloud point (caused by the UCST). (The cloud points are defined as the temperature at which a solution of the hotmelt adhesive clouds visibly to the eye.)

In a (preferred) embodiment, the water-soluble hotmelt adhesive has an upper cloud point of at least about 60°C in the form of a 0.3% by weight  
25 solution. The upper cloud point of a 1% by weight solution and more particularly a 3% by weight solution is preferably 60°C.

The lower cloud point should advantageously be below about 20°C for a 0.3% by weight solution of the hotmelt adhesive. The lower cloud point of a 1% by weight solution and more particularly a 3% by weight  
30 solution is preferably below about 20°C. For example, the lower cloud

point can be about 10°C or lower, about 5°C or about 3°C for the concentrations mentioned above.

In a preferred embodiment of the invention, the hotmelt adhesives used are miscible with water in virtually any quantity, i.e. there is no  
5 miscibility gap at concentrations of at least about 10% by weight or higher, for example about 20% by weight or about 50% by weight.

The hotmelt adhesives usable in accordance with the invention are generally solid and at least partly crystalline at room temperature. The degree of crystallization varies within wide limits according to the starting  
10 materials and the crystallization conditions. For example, it is at least about 20 to about 100% and, more particularly, at least about 30%, based on the degree of crystallization of polyethylene glycol 6000 (as measured by DSC). The hotmelt adhesives have a melting point of at least about 60°C or even, for example, about 70°C to about 100°C providing the melt  
15 has the required viscosities at the application temperature.

Even 100% amorphous systems may be used. However, their glass transition temperature (T<sub>g</sub>) should be at least about 30°C and preferably at least about 50°C.

The hotmelt adhesive is generally applied to the paper layers in  
20 molten form by conventional methods. Suitable methods of application are, for example, application by rollers, slot dies and spray nozzles.

If the hotmelt adhesive is applied by roller, only very high weights per unit area of adhesive can generally be achieved. Accordingly, roller application is normally used for firmly bonding the individual paper layers.  
25 Hotmelt adhesives suitable for application by roller are, for example, those with a melt viscosity at about 120 to about 150°C (Brookfield Thermocell, spindle 27) in the range from about 1,000 to about 6,000 mPa.s and more particularly in the range from about 2,000 to about 3,000 mPa.s. Moisture-tackifiable materials, for example, can be produced by roller application.

30 "Moisture-tackifiable" materials in the context of the invention are

understood to be materials which can be converted by moistening into self-adhesive systems. Such materials generally include materials which, on one side at least, have a layer which can be tackified by moistening with water and applied, for example, to a second material. After evaporation of the water, the materials adhere to one another. Examples of such materials are stamps, envelopes, labels and the like.

If the hotmelt adhesive is applied through a slot die, a hotmelt adhesive with a melt viscosity at about 120 to about 150°C (Brookfield Thermocell, spindle 27) in the range from about 400 to about 20,000 and more particularly in the range from about 600 to about 5,000 mPas is generally used for this purpose.

Application of the hotmelt adhesive by a spray nozzle is preferred for bonding tissues, the adhesive not being applied over the whole surface. The bonding of tissues can be carried out both by atomizing and by non-atomizing spray nozzles ("spin spraying").

Atomizing spray nozzles generally require a hotmelt adhesive which has a melt viscosity at about 120 to about 150°C (Brookfield Thermocell, spindle 27) in the range from about 400 to about 10,000 and more particularly in the range from about 600 to about 5,000 mPas. Non-atomizing spray nozzles require hotmelt adhesives with a slightly higher viscosity in order to guarantee the necessary filament cohesion, for example hotmelt adhesives with a melt viscosity at about 120 to about 150°C (Brookfield Thermocell, spindle 27) in the range from about 3,000 to about 10,000 mPa.s.

The present invention also relates to a process for the production of moisture-tackifiable materials in which a hotmelt adhesive with a solubility in water at about 20°C of at least about 3% by weight is applied to a material, more particularly to paper. The hotmelt adhesive is applied by spraying or rolling, more particularly using a roller.

The present invention also relates to the use of polyalkylene glycol



with a molecular weight of at least 1,000 and a solubility in water at about 20°C of at least about 3% by weight as a hotmelt adhesive, more particularly for the production of at least two-ply hygiene papers or moisture-tackifiable materials.

- 5        The present invention also relates to the use of a nonionic polyurethane with a molecular weight ( $M_n$ ) of at least 2,000 as a hotmelt adhesive, more particularly for the production of at least two-ply hygiene papers or moisture-tackifiable materials.

The process according to the invention is illustrated by the following

- 10    Examples.

### Examples

#### Production of the hotmelt adhesives

- 15    Example 1

97.3 parts by weight of polyethylene glycol with an OH value of 19 (PEG 6000) were freed from water for 2 hours at 90°C/1 mbar pressure. After addition of 2.7 parts by weight of TMXDI, the reaction temperature was increased under nitrogen to 140°C. After a reaction time of about 2  
20    hours, the NCO value was 0%. The substance had a melt viscosity of ca. 5,500 mPa.s at 150°C.

#### Examples 2 to 5

- 25        The polyurethanes listed in Table 1 below were produced in the same way as described in Example 1.

Example No.	Composition	Parts by weight	Melt viscosity [mPa.s]
2	PEG 12000/TMXDI	98.8:1.2	39,400 (150°C)
3	PEG 12000/octadecane-1,12-diol/TMXDI	91.1:4.6:4.3	40,000 (150°C)
4	PEG 12000/octadecane-1,12-diol/TMXDI	90.9:4.6:4.5	71,000 (120°C)
5	PEG 1550/TMXDI	86.6:13.4	8,500 (150°C)
6	PEG 3000/octadecane-1,12-diol/TMXDI	86.4:4:9.6	12,800 (150°C)
7	PEG 3000/octadecane-1,12-diol/TMXDI	89.5:2:8.5	18,000 (150°C)
8	PEG 6000/octadecane-1,12-diol/TMXDI	89.1:4.1:6.8	16,000 (150°C)

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